Electronic Supplementary Information for

A noble-metal-free MoS₂ nanosheet-coupled MAPbI₃ photocatalyst for efficient and stable visible-light-driven hydrogen evolution

Fang Wang,^{a,b,c} Xiangyu Liu,^{a,b,c} Zhengguo Zhang^{a,b,c} and Shixiong Min^{*a,b,c}

^a School of Chemistry and Chemical Engineering, Key Laboratory of Electrochemical Energy Conversion Technology and Application, North Minzu University, Yinchuan 750021, China.

^{*b*} Key Laboratory of Chemical Engineering and Technology, State Ethnic Affairs Commission, North Minzu University, Yinchuan 750021, China.

^c Ningxia Key Laboratory of Solar Chemical Conversion Technology, North Minzu University, Yinchuan 750021, China.

1. Experimental

1.1 Chemicals and Materials

Methylammonium iodine (MAI, \geq 99.5%) and PbI₂ (\geq 99.99%) were obtained from Xi'an Polymer Light Technology Corp. HI (55-57 wt% in water) was purchased from Shanghai Titan Scientific Co. Ltd. H₃PO₂ (50 wt% in water) was received from Shanghai Aladdin Biochemical Technology Co. Ltd. Pt/C catalyst (60 wt.%) was purchased from Suzhou Yilongsheng Energy Technology Co. Ltd. (NH₄)₂MoS₄ was prepared according to a reported procedure.¹

1.2 Preparation of few-layer MoS₂ nanosheets (MoS₂ NSs)

Few-layer MoS₂ nanosheets were prepared according to a reported procedure. Bulk MoS₂ crystals were synthesized by thermal decomposition of $(NH_4)_2MoS_4$ in an N₂ atmosphere at 800 °C for 5 h with a ramping rate of 5 °C min⁻¹. Then, 100 mg of the as-prepared bulk MoS₂ crystals was added into a 100 mL glass vial containing 50 mL of methanol as the exfoliation and dispersion solvent. The mixture was bath sonicated for 48 h at a frequency of 40 kHz. The resulting suspensions were first centrifuged at 2000 rpm for 1 h, and the top 2/3 portions of the supernatants were carefully collected. The collected supernatants were then sonicated for another 4 h. Then, the exfoliated MoS₂ suspensions were collected by another centrifugation of the supernatant at 4000 rpm for 1 h, and freeze dried to obtain MoS₂ NSs powders.

1.3 Preparation of MAPbI₃ and MAPbI₃-saturated HI/H₃PO₂ solution

MAPbI₃ was synthesized by the reaction of MAI (2.56 g) and PbI₂ (7.43 g) in a 25 mL of mixed solution containing H₃PO₂ (50 wt %) and HI (57 wt %) at a volume ratio of 1:4. The solution was then heated at 100 °C for 1 h and cooled to room temperature to obtain the saturated solution with MAPbI₃ precipitates. The MAPbI₃ precipitates were separated from the saturated solution by centrifugation and dried at 60 °C for 48 h in a vacuum oven to get MAPbI₃ powders, and the obtained MAPbI₃-saturated HI/H₃PO₂ solution was preserved for photocatalytic experiments and photoelectrochemical measurements.

1.4 Preparation of MAPbI₃/MoS₂ NSs composite photocatalysts

MAPbI₃/MoS₂ NSs composite photocatalysts were synthesized by a simple solutionbased in situ coupling method. Specifically, 100 mg MAPbI₃ and several different amounts (1, 3, 5, and 7 mg) of MoS₂ NSs were added to a reaction cell (65 mL) containing 5 mL of MAPbI₃-saturated HI/H₃PO₂ solution. The resulting mixture solutions were ultrasonicated for 5 min. The MAPbI₃/MoS₂ NSs composite photocatalysts were then either collected by centrifugation for further characterizations or directly used for following photocatalytic H₂ evolution experiment.

1.5 Characterization

X-ray diffraction (XRD) patterns were investigated with a Rigaku Smartlab diffractometer with a nickel filtrated Cu Ka radiation. Scanning electron microscopy (SEM) images were taken with a ZEISS EVO 10 scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope. Atomic force microscopy (AFM) was carried out on a Bruker Dimension Icon atomic force microscope in tapping mode. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using an Al Ka X-ray source. Binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp² hybridized (C=C) carbon from the sample. Raman spectra were recorded with a DXR2xi Raman microscope (Thermo Fisher Scientific) with a 532 nm laser as excitation source at room temperature. UV-vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere and BaSO₄ powders were used as a reflectance standard. UV-vis absorption spectra were taken with a Thermo Scientific-Evolution 220 spectrophotometer. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. Surface photovoltage (SPV) measurements were recorded on a CEL-SPS1000 (Au-Light Co., Ltd) on the basis of the lock-in amplifier, including a lock-in amplifier (SR830, Stanford research systems, Inc.), monochromatic-light, a light chopper (SR540, Stanford research systems, Inc.), and a chamber. Monochromatic light was generated from a 150 W xenon lamp (CEL-S150) by a monochromator (CEL-IS151).

1.6 Photocatalytic H₂ evolution experiments

Photocatalytic H₂ evolution experiments were performed with a PCX50C Discover multichannel photocatalytic reaction system (Beijing Perfectlight Technology Co. Ltd.) with white-light LED lamps (10 W×9, 380 nm $\leq\lambda\leq$ 780 nm, 450 mW/cm²) as the light source. Then, the reaction solution was thoroughly degassed by repeated evacuation-N₂ filling, and finally refilled with N₂ to reach ambient pressure. After that, the reaction solution was irradiated under continuous stirring. The amount of H₂ produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a precalibrated gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm×5 m), and with N₂ as carrying gas.

1.7 Electrochemical and photoelectrochemical measurements

All the electrochemical photoelectrochemical measurements were carried out in a standard three-electrode electrochemical set-up using a CHI760E potentiostat. The saturated Ag/AgCl and Pt mesh (1 cm×1 cm) were used as reference electrode and counter electrode, respectively. For the fabrication of working electrode, the catalyst suspension was prepared by dispersing 20 mg of catalysts into 1 mL of MAPbI₃-saturated aqueous HI/H₃PO₂ mixed solution by ultrasonication for 30 min under N₂ atmosphere. Afterward, the as-prepared catalyst suspension was loaded onto carbon paper (HESEN, HCP030P, thickness, 0.3 mm). The loading amount of the catalysts on carbon paper was controlled to be 0.167 mg cm⁻². The polarization curves was obtained using linear sweep voltammetry (LSV) method at a scan rate of 10 mV s⁻¹ in a MAPbI₃-saturated aqueous HI/H₃PO₂ mixed solution.

For photocurrent measurements, a Pt mesh (1 cm×1 cm) and a saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. A 30 mL of MAPbI₃-saturated aqueous HI/H₃PO₂ mixed solution was used as the supporting electrolyte, which was degassed with N₂ (40 mL min⁻¹) for 10 min before the test. A 30-W white LED lamp equipped with a cut-off filter of 420 nm was used as the light

source. Photocurrents were collected by an inert Pt mesh $(1 \text{ cm} \times 1 \text{ cm})$ as the working electrode $(1 \text{ cm} \times 1 \text{ cm})$ immersed in an aqueous suspension of photocatalyst (50 mg). Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were carried out with an AC amplitude of 5 mV in the frequency range of 10 mHz to 100 kHz.

2. Additional data



Fig. S1 Comparison of XRD patterns of bulk MoS₂ crystals and exfoliated MoS₂ NSs.



Fig. S2 (a) The photograph showing the Tyndall light scattering of obtained MoS_2 nanosheet dispersions in in methanol and (b) UV-Vis absorption spectra of MoS_2 nanosheet dispersions in methanol.



Fig. S3 AFM image and height profiles of exfoliated MoS₂ NSs.



Fig. S4 (a, b) TEM and (c, d) HRTEM images of the $MoS_2 NSs$.



Fig. S5 XRD patterns of (a) pristine MAPbI₃, (b) MoS₂ NSs, (c) MAPbI₃/MoS₂ NSs (1 mg), (d) MAPbI₃/MoS₂ NSs (3 mg), (e) MAPbI₃/MoS₂ NSs (5 mg), and (f) MAPbI₃/MoS₂ NSs (7 mg).



Fig. S6 (a, b) SEM images and (c, d) TEM images of the MAPbI₃.



Fig. S7 XPS survey spectrum of pristine $MAPbI_3$, $MoS_2 NSs$, and $MAPbI_3/MoS_2 NSs$

composite.



Fig. S8 XPS spectra (a) Pd 4f and (b) I 3d of pristine MAPbI₃ and MAPbI₃/MoS₂ NSs composite. XPS spectra (c) Mo 3d and (d) S 2p of MoS₂ NSs and MAPbI₃/MoS₂ NSs composite.

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Catalyst	Reactant solution	Light source	H_2 evolution activity (H_2 , µmol h ⁻¹)	Stability	Ref.
MAPbI ₃ /MoS ₂ NSs	HI solution	10 W LED lamp (380 nm≤λ≤780 nm)	206.1	>150 h	This work
MAPbI ₃ /Pt/C	HI solution	10 W LED lamp (380 nm≤λ≤780 nm)	68.5	N/A	This work
MAPbI ₃ /Pt	HI solution	Solar simulator $(\lambda \ge 475 \text{ nm})$	11.4	160 h	2
MAPbI ₃ /rGO	HI solution	300 W Xe lamp ($\lambda \ge 420$	93.9	200 h	3
MAPbI ₃ /Ni ₃ C	HI solution	300 W Xe lamp (λ≥420 nm)	116.3	200 h	4
MAPbI ₃ /BP	HI solution	300 W Xe lamp ($\lambda \ge 420$	748.4	200 h	5
MAPbI ₃ /Pt/TiO ₂	HI solution	300 W Xe lamp (λ≥420 nm)	72.8	12 h	6
Hollow MoS ₂ /g-C ₃ N ₄ hybrids	Lactic acid (10 vol%)	300 W Xe lamp ($\lambda \ge 420$	26.8	16 h	7
MoS ₂ /pyridine- modified g-C ₃ N ₄ , 50 mg	Triethanolamin e (10 vol%)	300 W Xe lamp ($\lambda \ge 420$ nm)	25	25 h	8
a-MoS _x /g-C ₃ N ₄	Lactic acid (10 vol%)	3 W LED (λ≥420 nm)	13.7	12 h	9
CdS/MoS ₂	Lactic acid (10 vol%)	300 W Xe lamp (λ≥420 nm)	540	N/A	10
CdS/Co-MoS _x	Lactic acid (10 vol%)	300 W Xe lamp (λ≥420 nm)	535	36 h	11
		N/A	Dhi /Mag Nga at	Hor	

Table S1 Comparison of cocatalytic performance of MoS_2 NSs with recently reportedcocatalysts developed for MAPbI3 under visible light irradiation.



Fig. S9 XRD patterns of MAPbI₃/MoS₂ NSs before and after 156 h of photocatalytic H_2 evolution.



Fig. S10 (a, b) SEM and (c, d) TEM images of the MAPbI₃/MoS₂ NSs after 156 h of photocatalytic H₂ evolution.



Fig. S11 XPS spectra of Pb 4f, I 3d, Mo 3d, and S 2p of the MAPbI₃/MoS₂ NSs after 156 h of photocatalytic H₂ evolution.

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